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### ON THE REACTION OF DISULFIDES WITH CHLORAMINE-T IN ALCOHOLIC SOLVENTS. A REEXAMINATION

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## ON THE REACTION OF DISULFIDES WITH CHLORAMINE-T IN ALCOHOLIC SOLVENTS. A REEXAMINATION

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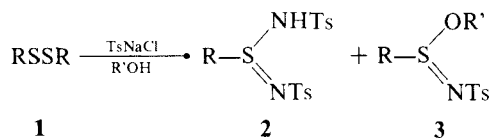
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Disulfides react with chloramine T in alcohols to give a mixture of *N*-tosylamides and alkyl esters of *N*-tosylalkane- or *N*-tosylarene-sulfinimidic acids.

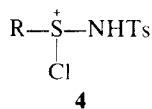
As a part of our researches on the chemistry of organic sulfur compounds,<sup>1</sup> we studied the reaction of dialkyl and diaryl disulfides (**1**) with chloramine T in some alcoholic solvents.

It has been reported by many authors<sup>2,3</sup> that such reaction affords exclusively *N*-tosylamides of *N*-tosylalkane- or *N*-tosylarene-sulfinimidic acids (**2**). However we could find that, besides (**2**), the esters (**3**), relative to the alcohol used as solvent, are also formed in comparable and sometimes higher yields. The yields,<sup>4</sup> physical constants and <sup>1</sup>H NMR data are summarized in the Table.



It is worth emphasizing that: (a) the (**2**) to (**3**) relative yields are greatly dependent on the nature of the disulfide and of the alcohol as well as on the reaction temperature (entries 6 and 7); (b) using Bu'OH as solvent there is no formation of ester (in **3** R = Bu'); (c) control experiments showed that compounds (**2**) and (**3**) are not interconverted and are stable under the reaction conditions.

In our opinion, from a mechanistic point of view, the formation of sulfinimidates (**3**) supports the course suggested by Campbell and Johnson<sup>3</sup> for the reaction of chloramine T with disulfides or with thiols (which presumably are first oxidized to disulfides). The proposed intermediate (**4**) can in fact react with TsNH<sup>-</sup> to give (**2**)



or undergo alcoholysis to (**3**). The lack of formation of ester when the reaction is carried out in the sterically hindered Bu'OH is in agreement with such hypothesis.

From a synthetic view-point, finally, the studied reaction can be considered a convenient "one-pot" method, alternative to those reported in literature,<sup>5</sup> for the preparation of esters of type (**3**).

TABLE I  
 Yields, Physical Constants and Spectral Data for Compounds (2) and (3)

Entry	R	R'	(2) <sup>a</sup> yield <sup>b</sup> (%)	yield <sup>b</sup> (%)	m.p. (°C) solvent	(3) <sup>a</sup> <sup>1</sup> H NMR (CDCl <sub>3</sub> , TMS) δ (p.p.m.), J in Hz
1	Et	Et	30 <sup>c</sup>	26	51–52 EtOH	7.79 and 7.25 (2H each, AA'BB', J 8.5), 4.07 (2H, app. q, J 7.1), 3.10 (2H, app. q, J 7.4), 2.39 (3H, s), 1.26 (3H, t, J 7.1) and 1.21 (3H, t, J 7.4).
2	Et	<i>s</i> -Bu	34 <sup>c</sup>	23	oil <sup>d</sup>	7.78 and 7.23 (2H each, AA'BB', J 8.5), 4.38 (1H, m), 3.08 (2H, app. q, J 7.4), 2.38 (3H, s), 1.57 (2H, m), 1.23 (6H, m) and 0.90 and 0.86 (3H in all, two overlap, t's).
3	PhCH <sub>2</sub>	Et	31 <sup>e</sup>	40	87–88 MeOH	7.51 and 7.08 (2H each, AA'BB', J 8.3), 7.23 (5H, bs), 4.34 (2H, AB, J 13.0), 4.10 (2H, app. q, J 7.0), 2.35 (3H, s) and 1.23 (3H, t, J 7.0).
4	PhCH <sub>2</sub>	<i>s</i> -Bu	37 <sup>e</sup>	31	oil <sup>d</sup>	7.51 and 7.08 (2H each, AA'BB', J 8.4), 7.23 (5H, bs), 4.33 (3H, m), 2.35 (3H, s), 1.52 (2H, m), 1.27 and 1.11 (3H in all, two d's, J 6.4) and 0.89 and 0.75 (3H in all, two overlap, t's, J 7.0).
5	Ph	Me	12 <sup>f</sup>	58	47–48 MeOH	7.81 (4H, m), 7.57 (3H, m), 7.24 (2H, BB' of AA'BB', J 8.2), 3.37 (3H, s) and 2.39 (3H, s).
6 <sup>g</sup>	Ph	Et	33 <sup>f</sup>	38	49–50 LP <sup>h</sup>	<sup>1</sup> 7.80 (7H, m), 7.35 (2H, BB' of AA'BB', J 7.8), 3.85 (2H, AB of ABX <sub>3</sub> ), <sup>j</sup> 2.39 (3H, s) and 1.12 (3H, t, J 7.0).
7 <sup>k</sup>	Ph	Et	30 <sup>f</sup>	65		
8	Ph	<i>t</i> -Bu	68 <sup>f</sup>	0		
9	4-MeC <sub>6</sub> H <sub>4</sub>	Et	32 <sup>l</sup>	65	58–59 EtOH	7.85 (2H, AA' of AA'BB', J 8.2), 7.68 (2H, AA' of AA'BB', J 8.4), 7.29 (4H, overlap, BB' parts), 3.79 (2H, AB of ABX <sub>3</sub> ), <sup>j</sup> 2.41 and 2.38 (3H each, s) and 1.11 (3H, t, J 7.1).
10	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	Et	23 <sup>m</sup>	22	80–81 <sup>n</sup> Et <sub>2</sub> O	
11	Mes <sup>o</sup>	Et	— <sup>p</sup>	56	100–102 EtOH	7.79 and 7.20 (2H each, AA'BB', J 8.4), 6.88 (2H, bs), 4.20 (2H, app. q), 2.54 (6H, s), 2.36 and 2.26 (3H each, s) and 1.31 (3H, t, J 7.1).

<sup>a</sup> All compounds gave satisfactory elemental analysis; <sup>b</sup> see note four; <sup>c</sup> m.p. 185–186° from EtOH (lit. <sup>2c</sup> 186–187.5°); <sup>d</sup> diastereomeric mixture; <sup>e</sup> m.p. 170–171° from EtOH (lit. <sup>2c</sup> 171–171.5°); <sup>f</sup> m.p. 152–153° from EtOH (lit. <sup>2a</sup> 152–153°); <sup>g</sup> reaction carried out at room temp.; <sup>h</sup> light petroleum b.p. 60–80°; <sup>i</sup> spectrum in CD<sub>3</sub>COCD<sub>3</sub>; <sup>j</sup> see ref. 7; <sup>k</sup> reaction carried out at 70°; <sup>l</sup> m.p. 149° from EtOH (lit. <sup>8</sup> 149°); <sup>m</sup> m.p. 165–166° from EtOH, δ (CD<sub>3</sub>COCD<sub>3</sub>) 8.45 and 8.07 (2H each, AA'BB', J 9.0 Hz), 7.71 and 7.32 (4H each, AA'BB', J 8.3 Hz) and 2.42 (6H, s); <sup>n</sup> lit. <sup>5a</sup> m.p. 79–80°; <sup>o</sup> Mes = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>; <sup>p</sup> the oily material was difficult to purify. The NMR analysis showed this was a mixture of at least two products which were not further investigated.

From the reaction of *p*-ditolyl disulfide with chloramine T in *l*-menthol, for instance, the two diastereomeric menthyl *N*-tosyl-*p*-toluenesulfonimides (in **3** R = *l*-menthyl), useful intermediates for the synthesis of chiral sulfimides,<sup>5b</sup> could be obtained in *ca.* 15% yield, which is comparable to that reported for a more troublesome three step procedure.<sup>5b</sup>

## EXPERIMENTAL

$^1\text{H}$  NMR spectra were taken on a Varian FT 80 instrument ( $\text{SiMe}_4$  as internal reference). Melting points are uncorrected. Column chromatography was performed with Merck silica gel of particle size 0.05–0.2 mm. Reagents and solvents were purchased from standard commercial sources and when necessary purified to match literature physical data. Disulfides were either purchased or prepared according to literature procedures and purified to match reported physical and spectral data.

*General Procedure for Performing the Reactions between Disulfides and Chloramine T*

Chloramine T (4 mmol) was added at  $40^\circ$  to a mechanically stirred solution of disulfide (1 mmol) in alcohol (5 mL). The reaction solution was slowly warmed to  $70^\circ$  (over ca. 20 min) and kept at this temperature for further 10 min. The alcohol was evaporated and the residue extracted by decantation with  $\text{Et}_2\text{O}$  ( $2 \times 30$  mL).<sup>6</sup> The insoluble material was taken up with water acidified with HCl. Filtration gave sulfinimidamides (**2**) which were purified by crystallization from the proper solvent (see Table). The ether extracts were washed with 10% NaOH solution, water, dried and evaporated to leave crude alkyl sulfinimidates (**3**), which were purified by column chromatography (silica gel/ $\text{CHCl}_3$ ).

## REFERENCES AND NOTES

1. C. Dell'erba, G. Guanti, G. Garbarino, M. Novi and G. Poluzzi Corallo, *Tetrahedron*, **37**, 795 (1981).
2. (a) S. G. Clarke, J. Kenyon and H. Phillips, *J. Chem. Soc.*, 1225 (1930); (b) J. R. Alexander and H. McCombie, *J. Chem. Soc.*, 2087 (1932); (c) G. Bullmer and F. G. Mann, *J. Chem. Soc.*, 666 (1945); (d) G. E. Dalglish and F. G. Mann, *J. Chem. Soc.*, 913 (1945).
3. M. M. Campbell and G. Johnson, *Chem. Rev.*, **78**, 65 (1978).
4. The yields, based on (**1**), were normalized assuming as 100% yield the formation of 2 moles of (**2**) or (**3**) per mole of (**1**). No attempt was made to optimize these yields.
5. (a) E. S. Levchenko and L. V. Seleznenko, *Zhur. org. Khim.*, **2**, 890 (1966); (b) T. R. Williams, A. Nudelman, R. E. Booms and D. J. Cram, *J. Amer. Chem. Soc.*, **94**, 4684 (1972).
6. As regards the reaction in *l*-menthol, the reaction mixture, after cooling, was taken up with  $\text{Et}_2\text{O}$ . The insoluble material was filtered and worked up as reported. From the filtrate the solvent and the menthol were distilled off under reduced pressure (20 mm and then 3 mm Hg at ca.  $50^\circ$ ) to give crude ester **3** ( $\text{R} = l$ -menthyl).
7. F. A. Bovey, *Nuclear Magnetic Resonance Spectroscopy* (Academic Press, New York, 1969), p. 161.
8. G. Leandri and D. Spinelli, *Ann. Chim. (Italy)*, **49**, 964 (1959).